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The effect of pressure on the Morin transition in hematite (α-Fe_2O_3)

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Abstract

Neutron powder scattering studies of hematite to a pressure (P) of 6.2 GPa in a Paris–Edinburgh (PE) cell with Fluorinert® as a P-transmitting medium, reveal different behavior to previous investigations that used solid pressure-transmitting media. The P equivalent of the Morin transition is closely approached at room temperature at the highest P. In the present study the spin reorientation, from perpendicular to parallel to the rhombohedral [1 1 1] direction, begins at some 3 GPa higher and goes 25° beyond what was previously observed at high P.

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1. Introduction

Experimental determinations of the magnetic properties of 'simple' transition metal oxides, and their solid solutions, as a function of pressure (P) and temperature (T) have implications for magnetic transitions of importance to the Earth's crust and interior. Hematite is important in paleomagnetism and its natural remnant magnetization (NRM) is widely used in red sediments [1]. There is evidence of a particle size dependence [1] to the magnetization, which is still of topical interest, and general agreement that the NRM is not due solely to impurities but to intrinsic anisotropic superexchange interactions [2] giving rise to weak ferromagnetism due to canting.

The structural and magnetic properties of hematite (α-Fe_2O_3) as a function of T are well known [3]. At ambient PT the nuclear structure is rhombohedral (shown in Fig. 1 in the hexagonal setting) and related to that of corundum (Al_2O_3). The magnetic structure at ambient PT was determined using neutron powder diffraction (NPD) by Shull et al. [3] who found spins on the Fe atoms are aligned ferromagnetically within each of the basal layers. Spins between layers are coupled antiferromagnetically [3] along the c-axis, equivalent to the rhombohedral [1 1 1] direction used in the literature [3]. Below 250 K, at the Morin transition [4], the NPD [3] pattern can be accounted for on the basis of an antiferromagnetic lattice with iron spins oriented along the $[1\,1\,1]_{\mathrm{rhombohedral}}$ ($= c_{\mathrm{hexagonal}}$) direction (Fig. 1). The spin flop transition, with the change in moment direction from within the basal plane to perpendicular to it, is seen readily in the relative intensities of the first two magnetic peaks. The $(1\,1\,1)_M$ and $(1\,0\,0)_M$ are both pure magnetic reflections and the $(1\,1\,0)_N$ is of pure nuclear origin [3]. As T is lowered at ambient P toward the Morin transition, the $(1\,1\,1)_M$ disappears. The moment strength and direction can be readily detected by measuring the relative intensities of these first 3 reflections in the NPD pattern (Fig. 2). Rietveld structure refinement is a convenient way to obtain the variation in moment along with the nuclear structure.

The effect of P on the Morin transition has been studied [5] from ambient P and up to 10 GPa. A rapid increase in the Morin transition T of about 3 °/kbar

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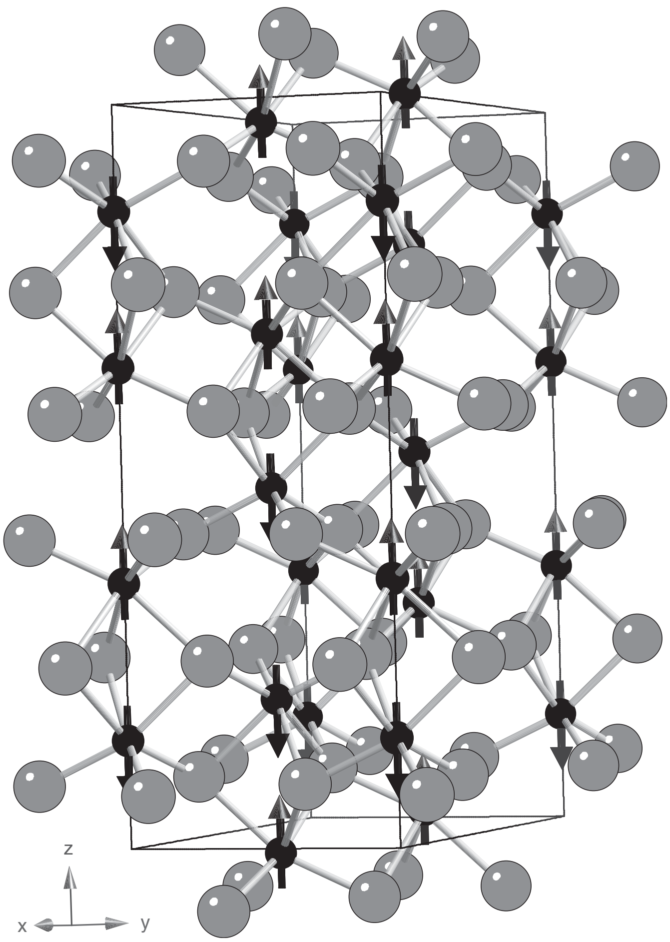

Fig. 1. Structure of hematite (α-Fe_2O_3) in the hexagonal setting with vectors indicating spin directions oriented along the $c_{hexagonal}$ ($=[1\,1\,1]_{rhombohedral}$) direction below the Morin transition at ~250 K and above 7 GPa (Figs. 2 and 3). Small black and large gray spheres indicate iron and oxygen, respectively.

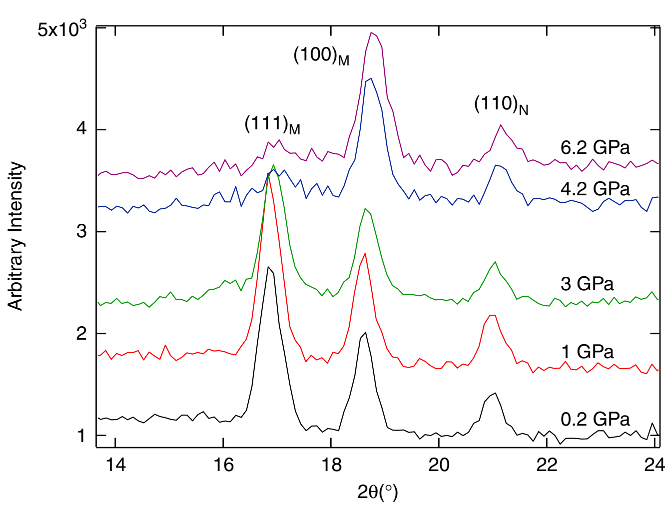

Fig. 2. Low-angle data collected at the Chalk River reactor showing the magnetic (M) and nuclear (N) peaks for hematite. The indexing is with respect to the rhombohedral setting of the hexagonal unit cell shown in Fig. 1, consistent with previous studies [2–5]. The equivalent peaks in the hexagonal setting, starting with the rhombohedral $(1\,1\,1)_M$ are (0 0 3), (1 0 1) and (1 0 2) in the hexagonal setting.

(1 kbar = 0.1 GPa) is found below 0.6 GPa in a hydrostatic environment [6] suggesting the Morin transition should reach room temperature at about 1.5 GPa. Later experiments [5] with P of 10 GPa show that this rate is not maintained. In studies carried out in a non-hydrostatic environment, without pressure-transmitting media, the Morin transition was not complete at 10 GPa and reorientation of the spin did not occur at 4.9 GPa even when hematite was cooled below 50 K [5]. Goncharenko et al. [5] speculated that the stability of the ratio of the magnetic intensities above 3 GPa, both at high P and at variable T, suggests a new magnetic phase, with a moment direction intermediate between those above and below the Morin transition, is stable under these conditions. Some of these effects could be due to deviatoric stress. No special pressure-transmitting media were used in the powder diffraction experiments and a distribution of P would be expected within the sample, with high P gradients and a population of grains 'feeling' much less P than 10 GPa.

We decided to test the hypothesis that deviatoric stress was the cause of the incomplete spin flip transition at high P by using Fluorinert® in a Paris–Edinburgh (PE) cell [7] at the Chalk River reactor. Although Fluorinert® is solid above 4 GPa we observe *almost* complete disappearance of the $(1\,1\,1)_M$ about 6 GPa. This strongly suggests that indeed deviatoric stress does hinder the transition and that, were the experiment carried out under truly hydrostatic conditions, the transition would be observed at P lower than 6 GPa. This result has implications for the magnetization of natural hematite in the earth.

2. Experimental

The sample of hematite used was commercially available iron(III) oxide, powder from Aldrich Corporation (product number 544884-25G) with a nominal average particle size 20–50 nm. Pressure was generated by a PE cell fitted with two toroidal anvils deforming a metallic gasket which contains a sample volume of about 80 mm^3 [7–9].

Unlike the standard PE setup, incident and scattered beams are in the equatorial plane for angular dispersive measurements, rather than having the incident beam transmitted through the back of the upstream anvil and scattered at 90° through the TiZr metal gasket, as is the geometry for measurements at spallation sources. An excellent description of the setup for AD measurements is provided in a recent publication [8]. For our AD measurements we used standard WC anvils, which need to be 'dressed' with Cd-foil to minimize parasitic scattering from steel and WC in the anvils. This can be avoided by using BN anvils [8,10] but at the expense of limiting scattering from the roughly spherical sample to the slit between the BN anvils. We chose to maximize sample scattering since contamination from the steel and WC occur far from the magnetic peaks of interest.

The PE cell was mounted on the C2 diffractometer at Chalk River. A wavelength of 1.3290 Å, was taken from

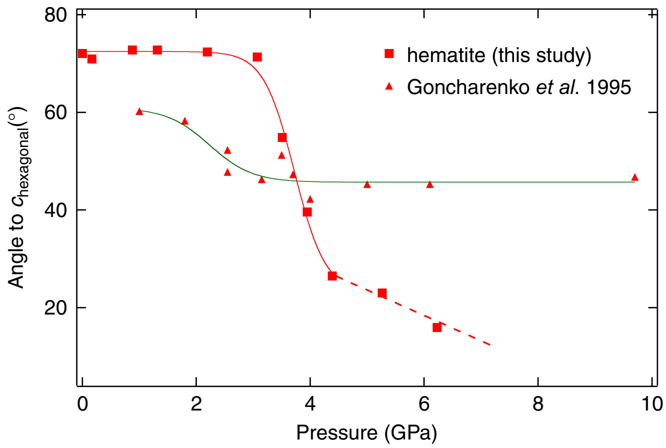

Fig. 3. Variation with P of the angle between the moment vector and the c-axis for the hexagonal cell (rhombohedral [1 1 1]) shown in Fig. 1 (squares are for this study and triangles are data taken from the work of Goncharenko et al. [5]). The lines are guides to the eye.

a planar Si (5 3 1) monochromator at 92.7° $2\theta_m$. The wavelength was calibrated using an external NIST powder Si 640c position standard. The instrument consists of an 800-wire BF_3 multidetector, which floats over an epoxy dance floor. A P calibration of the PE cell was performed by measuring the cell parameters of pure NaCl, over the same P range as the hematite data, with reference to the NaCl equation of state [11]. The diffraction data were fit using Winplotr [12]. A four-phase fit was performed describing the nuclear and magnetic structure of hematite, as well as a basic description of the parasitic scattering from steel and WC. The magnetic moment orientation was described in a model using spherical polar coordinates.

The magnetic structure for hematite was first refined using data collected at ambient PT in a vanadium can. Trial refinements converged on a cant angle of 72° to the $c_{hexagonal}$ axis for a moment 3.9 μ_B; the refined value of the moment magnitude refined for all data sets to close to this value and was fixed through out. Data collected at high Ps (Fig. 2) clearly show a decrease in the $(1\,1\,1)_M$ peak indicative of the moment direction approaching $[1\,1\,1]_{rhombohedral}$.

3. Results and discussion

The relevant results of Rietveld refinements are summarized in Fig. 3 where the moment angles as a function of P found for our study of hematite are compared to those of Goncharenko et al. [5].

Several points emerge from consideration of the results of this study and those of previous workers [4–6]: the behavior of hematite at high P is quite different in different pressure media [5]. The magnetic moment for hematite in Fluorinert® (F-hematite) remains close to that determined at ambient PT until about 3.5 GPa, while the moment does not change in hematite above 4 GPa when it is pressurized without pressure medium [5]. For F-hematite the moment continues to move closer to the c-axial direction above 4 GPa (Fig. 3) and, if the trend predicted by the dotted line in Fig. 3 were to continue, the Morin transition (Fig. 1) should reach room T at about 10 GPa.

The observations of the P dependence of the moment direction (Fig. 3) suggest dependence on deviatoric stress, P and possibly T that require more systematic characterization along with particle size dependence, and these studies are on going. The results obtained thus far demonstrate again how facile it is to use the PE cell on reactor sources [8,10] for magnetic studies and how rich the magnetic phenomena can be under high P conditions.

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References

[1] D.J. Dunlop, Science 169 (1970) 858.
[2] T. Moriya, Phys. Rev. 120 (1960) 91.
[3] C.G. Shull, W.A. Strauser, E.O. Wollan, Phys. Rev. 83 (1951) 333.
[4] F.J. Morin, Phys. Rev. 78 (1950) 819.
[5] I.N. Goncharenko, J.-M. Mignot, G. Andre, O.A. Lavrova, I. Mirebeau, V.A. Somenkov, High Press. Res. 14 (1995) 41.
[6] C.W. Searle, Phys. Lett. A 25 (1967) 256.
[7] J.M. Besson, S. Klotz, G. Hamel, I. Makarenko, R.J. Nelmes, J.S. Loveday, R.M. Wilson, W.G. Marshall, High Press. Res. 14 (1995) 1.
[8] S. Klotz, T. Strassle, G. Rousse, G. Hamel, Appl. Phys. Lett. 86 (2005).
[9] J.S. Loveday, R.J. Nelmes, W.G. Marshall, R.M. Wilson, J.M. Besson, S. Klotz, G. Hamel, S. Hull, High Press. Res. 14 (1995) 7.
[10] N. Kernavanois, T. Hansen, E. Ressouche, Y.J. Henry, T. Strässle, S. Klotz, G. Hamel, J.B. Parise, http://www.ill.fr/AR-03/site/02_scientific/021_magnetic/02_magn_10.htm (2002).
[11] F. Birch, J. Geophys. Res. 91 (1986) 4949.
[12] T. Roisnel, J. Rodriguez-Carvajal, WinPLOTR, a new tool for powder diffraction Saclay, France, 2000.